Synthesis and Reactions of Polycyclic Hydrocarbons

1. *o*-Toluoyl- and β-Methylnaphthoylphenanthrenes.
2. The Reaction of Alkali Metals with Polycyclic Hydrocarbons.

A DISSERTATION

SUBMITTED IN PARTIAL FULFILMENT OF THE REQUIREMENTS
FOR THE DEGREE OF DOCTOR OF PHILOSOPHY
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By
Leland Hadley Pence
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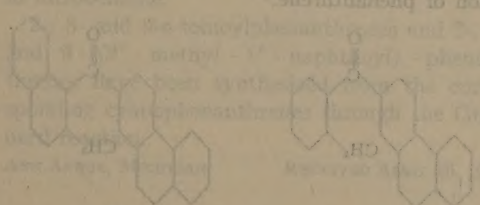
[CONTRIBUTION FROM THE CHEMISTRY LABORATORY OF THE UNIVERSITY OF MICHIGAN]

Synthesis of Phenanthrene Derivatives. III. o-Toluoyl- and β-Methylnaphthoyl-phenanthrenes[1]

By W. E. Bachmann and E. R. Peace

From the reaction between o-toluoyl chloride, phenanthrene and aluminum chloride in carbon disulfide Clar[2] obtained an uncrystallizable oil, from the nature of the compounds which resulted on pyrolysis of the oil, he concluded that his product contained 2-, 3-, and 9-o-toluoylphenanthrene, the 9-isomer being present in the largest proportion. Cook[3] likewise failed to obtain a crystalline product in his attempt to synthesize 3-o-toluoylphenanthrene by interaction of 3-phenanthroyl chloride and o-tolylmagnesium bromide. We have now found that if nitrobenzene is used as the solvent in the Friedel and Crafts reaction a mixture of 2-o-toluoylphenanthrene (I) and 3-o-toluoylphenanthrene is obtained which can be separated readily into its two crystalline components. These results are similar to those obtained recently in the benzoylation of phenanthrene.[4]



I II

The structures of these new ketones were established by synthesis; reaction of 2- and 3-cyanophenanthrene with o-tolylmagnesium bromide gave the ketone-imines, which were easily hydrolyzed to the ketones. We have also prepared 9-o-toluoylphenanthrene by this reaction; this isomer had been prepared previously from 9-phenanthroyl chloride and o-tolylmagnesium bromide and 9-phenanthronitrile.[5] These two methods now make 9-o-toluoylphenanthrene readily available for the preparation of 1,2,3,4-dibenzanthracene, the pyrolysis product of the ketone. Cook, Hieger, Kennaway and Mayneord[3] reported that they were uncertain whether 1,2,3,4-dibenzanthracene pos-

(1) From part of the Ph. D. dissertation of E. R. Peace.
(2) Clar, *Ber.*, **68**, 320, 1673 (1935).
(3) Cook, *J. Chem. Soc.*, 449 (1931).
(4) Backmann, *This Journal*, **57**, 555 (1935).
(5) Backmann, *ibid.*, **56**, 1853 (1934).
(6) Cook, Hieger, Kennaway and Mayneord, *Proc. Roy. Soc.* (London), **111A**, 455 (1926).

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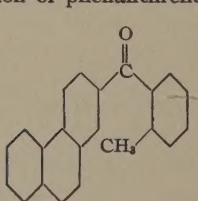
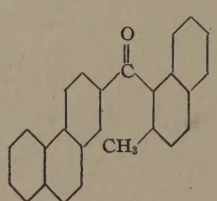


I



II

The structures of these new ketones were established by synthesis; reaction of 2- and 3-cyanophenanthrene with *o*-tolylmagnesium bromide gave the ketone-imines, which were easily hydrolyzed to the ketones. We have also prepared 9-*o*-toluoylphenanthrene by this reaction; this isomer had been prepared previously from 9-phenanthrylmagnesium bromide and *o*-tolunitrile.[5] These two methods now make 9-*o*-toluoylphenanthrene readily available for the preparation of 1,2,3,4-dibenzanthracene, the pyrolysis product of the ketone. Cook, Hieger, Kennaway and Mayneord[6] reported that they were uncertain whether 1,2,3,4-dibenzanthracene possessed cancer-producing properties, for most of their tests were made on impure specimens.

Since the 2-, 3- and 9-cyanophenanthrenes can be readily prepared,[7] the Grignard reaction offers one of the best methods for obtaining these pure ketones. We have used the reaction also to synthesize 2-(2′-methyl-1′-naphthoyl)-phenanthrene (II) and its 3- and 9-isomers; of these, the 3-isomer has been prepared previously by Cook[3] and the 9-isomer by Fieser and Dietz[8] by other methods. The ketone-imines which are obtained from the cyanophenanthrenes and the Grignard reagent from 2-methyl-1-bromonaphthalene are hardly affected when they are refluxed with dilute hydrochloric acid, presumably because of steric hindrance; complete hydrolysis to the ketones was effected at 200° in a sealed tube.

From the pure *o*-toluoylphenanthrenes and β-methylnaphthoylphenanthrenes we are preparing the polycyclic hydrocarbons that can be derived from them by pyrolysis. We are employing the Grignard reaction for making a large number of ketones for the purpose of obtaining polycyclic hydrocarbons and derivatives with carcinogenic properties.

Experimental

Reaction of *o*-Toluoyl Chloride with Phenanthrene.—To an ice-cold solution of 32 g. of aluminum chloride in 125 cc. of nitrobenzene was added a solution of 20 g. of phenanthrene in 50 cc. of nitrobenzene followed by 17 g. of *o*-toluoyl chloride. After being kept cold for two hours, the mixture was allowed to stand at room temperature for twelve hours and then hydrolyzed. The product which remained after the nitrobenzene had been removed by steam distillation was distilled under reduced pressure (200–265° at 3 mm.). The distillate was dissolved in a mixture of acetone and alcohol; on cooling, 5 g. of phenanthrene crystallized out. After the removal of the phenanthrene the chilled solution was "seeded" with crystals of synthetic 3-*o*-toluoylphenanthrene (prepared from 3-cyanophenanthrene). After several crops of the 3-isomer had been obtained, the mother liquor was "seeded" with synthetic 2-*o*-toluoylphenanthrene. After several recrystallizations of the various fractions there was obtained 6.08 g. (24%) of 3-*o*-toluoylphenanthrene and 0.85 g. (3.4%) of the 2-isomer.

2-*o*-Toluoylphenanthrene crystallizes in thin colorless plates from a mixture of acetone and alcohol; m. p.

(1) From part of the Ph.D. dissertation of L. H. Pence.

(2) Clar, *Ber.*, **62**, 350, 1574 (1929).

(3) Cook, *J. Chem. Soc.*, 499 (1931).

(4) Bachmann, This Journal, **57**, 555 (1935).

(5) Bachmann, *ibid.*, **56**, 1363 (1934).

(6) Cook, Hieger, Kennaway and Mayneord, *Proc. Roy. Soc.* (London), **B111**, 455 (1932).

(7) Mosettig and van de Kamp, This Journal, **54**, 3328 (1932); Bachmann, References 4 and 5.

(8) Fieser and Dietz, *Ber.*, **62**, 1827 (1929).

115–116°. The ketone gives a deep-red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.2; H, 5.4. Found: C, 88.8; H, 5.4.

3-*o*-Toluoylphenanthrene was obtained in clusters of thin colorless plates by recrystallization from 80% acetic acid; m. p. 89–90°. A deep-red color forms when the ketone is added to concentrated sulfuric acid.

Anal. Calcd. for $C_{22}H_{16}O$: C, 89.2; H, 5.4. Found: C, 88.8; H, 5.4.

Synthesis of *o*-Toluoylphenanthrenes.—To the Grignard reagent which had been prepared from 10 g. of *o*-bromotoluene in 20 cc. of ether was added 25 cc. of benzene and 4.3 g. of cyanophenanthrene (2-, 3- or 9-isomer). After the mixture had been refluxed for four hours, it was cooled and shaken with dilute acetic acid. Addition of concentrated hydrochloric acid to the ether–benzene layer precipitated the imine-hydrochloride as an oil which soon crystallized. The compound was hydrolyzed to the ketone when it was refluxed with water for several hours; the ketones were recrystallized twice from acetone–alcohol. The yields were: 2-*o*-toluoylphenanthrene, 48%; 3-*o*-toluoylphenanthrene, 79%; 9-*o*-toluoylphenanthrene, 83%.

Synthesis of β-Methylnaphthoylphenanthrenes.—To the Grignard reagent which had been prepared from 12.5 g. of 1-bromo-2-methylnaphthalene in 40 cc. of ether and 40 cc. of benzene was added 5 g. of cyanophenanthrene (2-, 3- or 9-isomer). After being refluxed for four hours, the mixture was shaken with dilute hydrochloric acid; the imine-hydrochloride, which precipitated and was filtered off, was hydrolyzed by 1 cc. of concentrated hydrochloric acid and 50 cc. of water in a sealed tube at 200° for six hours.

2-(2′-Methyl-1′-naphthoyl)-phenanthrene (II) was purified by recrystallization from acetone–alcohol and then from acetic acid; it crystallizes in fine colorless needles; yield, 73%. When heated slowly from room temperature the compound melts at 184–185°; however, the compound melts completely when the melting point tube is placed in a bath at 168–170°, the melt solidifies and remelts at 184–185°. The ketone gives a deep-red color with concentrated sulfuric acid.

Anal. Calcd. for $C_{26}H_{18}O$: C, 90.2; H, 5.2. Found: C, 89.7; H, 5.2.

3-(2′-Methyl-1′-naphthoyl)-phenanthrene was obtained as colorless prisms after recrystallization from acetone–alcohol, distillation under reduced pressure and finally recrystallization from acetic acid; yield, 51%; m. p. 148.5–149.5° (Cook reported 145–146° for the ketone obtained from 3-phenanthroyl chloride and 2-methyl-1-naphthylmagnesium bromide). A crimson color is formed when the ketone is added to concentrated sulfuric acid.

A 65% yield of 9-(2′-methyl-1′-naphthoyl)-phenanthrene was obtained after the ketone had been recrystallized from toluene and twice from acetone; m. p. 176–177° (Fieser and Dietz gave 170° for the ketone made from 9-phenanthroyl chloride and 2-methyl-1-naphthylmagnesium bromide). The ketone crystallizes in clusters of thin sheets and gives a red color with concentrated sulfuric acid.

Summary

2- and 3-*o*-toluoylphenanthrenes have been isolated from the reaction between *o*-toluoyl chloride, phenanthrene and aluminum chloride in nitrobenzene.

2-, 3- and 9-*o*-toluoylphenanthrenes and 2-, 3- and 9-(2′-methyl-1′-naphthoyl)-phenanthrenes have been synthesized from the corresponding cyanophenanthrenes through the Grignard reaction.

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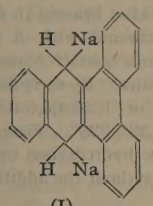
[Contribution from the Chemistry Laboratory of the University of Michigan]

The Reaction of Alkali Metals with Polycyclic Hydrocarbons. II

By W. E. Bachmann and L. H. Pence[1]

It was shown recently that sodium and lithium add to the *meso* positions of 1,2-benzanthracene, 1,2,5,6-dibenzanthracene and 3-methylcholanthrene.[2] We have now extended this reaction to include 5-methyl-1,2-benzanthracene, 5-phenyl-1,2-benzanthracene, 1,2,3,4-dibenzanthracene, 6-methyl-1,2,3,4-dibenzanthracene, 1,2,6,7-dibenzanthracene and 1,2,3,4,5,6-tribenzanthracene. Intensely colored addition compounds are formed when solutions of these hydrocarbons in ether–benzene are shaken with sodium or with lithium. Thus, 1,2,3,4-dibenzanthracene gives an intensely lavender colored solution of 9,10-disodium-9,10-dihydro-1,2,3,4-dibenzanthracene (I), while with lithium the intensely purple 9,10-dilithium addition product is formed.



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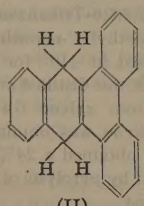
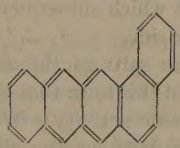


(II)

As a rule the color of the disodium addition product is different from that of the dilithium derivative. This difference is ascribed to a difference in the mode of addition of the two metals, the one adding in *cis* positions, the other in *trans* positions. On treatment with methanol, the alkali addition products of the hydrocarbons yield the 9,10-dihydro derivatives (II, for example). The same dihydro derivative is obtained from both the disodium and the dilithium addition compounds, except in the case of 1,2,6,7-dibenzanthracene (III). In the reaction between the alkali metals and 1,2,6,7-dibenzanthracene it was expected that addition could take place at the 5,8- or the 9,10-positions. Actually, a mixture of the two possible dihydro derivatives was obtained from the sodium addition product and methanol. A single dihydro compound was isolated from the dilithium addition product, although the structure of this compound was not determined.

The structures assigned to the dihydro derivatives and hence to the alkali metal addition products are based on the oxidation of the dihydro derivatives to the 9,10-diones by chromic acid. All of the 9,10-dihydro derivatives are dehydrogenated readily by sulfur to the parent hydrocarbons.

In order to obtain water-soluble derivatives of the polycyclic hydrocarbons, we have investigated the action of carbon dioxide on a number of the alkali addition products. In this reaction a distinct difference in behavior was encountered



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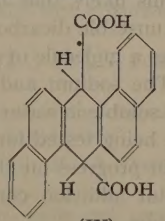

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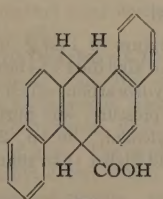

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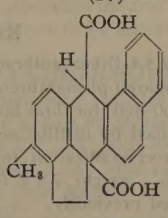

(VI)

(1) From the Ph.D. dissertation of L. H. Pence.

(2) Bachmann, *J. Org. Chem.*, **1**, 347 (1936).

between the disodium and the dilithium addition compounds. Thus, while the dilithium compound obtained from 1,2,5,6-dibenzanthracene yielded the expected dilithium salt of 9,10-dicarboxy-9,10-dihydro-1,2,5,6-dibenzanthracene (IV) exclusively, the disodium compound behaved in an erratic manner, not always giving the same compound even when the identical conditions appeared to be employed. Usually the monocarboxylic acid (V) was obtained from the disodium compound. The dicarboxylic acid (VI) was obtained from the dilithium addition product of 3-methylcholanthrene, the disodium compound yielding a monocarboxylic acid. A similar result was obtained with 1,2,3,4-dibenzanthracene.

From the reaction between carbon dioxide and the sodium addition compound of anthracene, Schlenk and Bergmann[3] isolated a dicarboxylic acid. When, however, anthracene was added to the disodium addition compound prior to the introduction of carbon dioxide, a monocarboxylic acid was formed; the latter compound was also obtained when the reaction between the anthracene and sodium had been incomplete. The excellent yields of dihydro compounds obtainable from our sodium addition compounds by reaction with methanol precluded an explanation of the formation of a monocarboxylic acid on the basis of an incomplete reaction between the hydrocarbon and sodium. Moreover, none of the parent hydrocarbon was isolated from the reaction mixture after treatment with carbon dioxide. It seems likely that the disodium compound yields an unstable dicarboxylic acid which subsequently loses a molecule of carbon dioxide.

The sodium and potassium salts of the acids are soluble in water and it is in this form that they are being tested for carcinogenic activity. Work is in progress on the reaction between the alkali metal addition compounds and alkyl and acyl halides.

Experimental

1,2,3,4-Dibenzanthracene.—A mixture of 14.8 g. of 9-(*o*-toluoyl)-phenanthrene[4] and 5 g. of zinc dust was heated at 400–420° for three hours. The hydrocarbon, which was obtained by distillation at 2 mm. pressure, was purified by recrystallization from xylene–alcohol; m. p. 200–201.5°; weight, 7.8 g. (56%), a yield higher than that reported previously.

6-Methyl-1,2,3,4-dibenzanthracene.—To the Grignard reagent prepared from 30 g. of 1-bromo-2,4-dimethylbenzene[5] in 50 cc. of ether was added 100 cc. of benzene and 30 g. of 9-cyanophenanthrene. After being refluxed for two days, the mixture was hydrolyzed with ice-cold hydrochloric acid, which precipitated a solid ketone imine hydrochloride. The ketone, 9-(2′,4′-dimethylbenzoyl)-phenanthrene, resulting from the hydrolysis of the ketone-imine hydrochloride by boiling water, was obtained as a colorless oil by distillation at 200–250° at 3 mm.; weight, 34 g. (75%).

The aforementioned ketone was kept at 420° for two and one-half hours and the product was distilled at 3 mm. pressure. Two recrystallizations from xylene, using decolorizing charcoal, gave 4.0 g. (12%) of 6-methyl-1,2,3,4-dibenzanthracene as fine, colorless needles; m. p. 157.5–158°. The hydrocarbon is only slightly soluble in cold alcohol and acetic acid.

Anal. Calcd. for $C_{23}H_{16}$: C, 94.5; H, 5.5. Found: C, 94.6; H, 5.5.

6-Methyl-1,2,3,4-dibenzanthraquinone was formed by refluxing a mixture of 100 mg. of the hydrocarbon, 200 mg. of sodium dichromate dihydrate and 10 cc. of acetic acid for thirty minutes. After sublimation at 230–260° (0.2 mm.), the quinone crystallized from acetic acid in long yellow needles; yield 65%; m. p. 187.5–188.5°.

Anal. Calcd. for $C_{23}H_{14}O_2$: C, 85.7; H, 4.4. Found: C, 85.2; H, 4.6.

1,2,6,7-Dibenzanthracene.—This hydrocarbon has been prepared previously but not from crystalline 3-(*o*-toluoyl)-phenanthrene. By heating a mixture of 6.6 g. of the crystalline ketone[4] and 2.2 g. of zinc dust at 400–420° for two hours, distilling the product at 3 mm. pressure and recrystallizing the distillate twice from xylene, 1.34 g. of 1,2,6,7-dibenzanthracene was obtained as golden-yellow crystals. The highest melting point which we observed was 262°, while Clar[6] reported a value of 263–264°.

1,2,3,4,5,6-Tribenzanthracene.—After heating 15.4 g. of 9-(2′-methyl-1′-naphthoyl)-phenanthrene[4] with 5 g. of zinc dust at 410° for two and three-quarter hours, the product was distilled at 3 mm. pressure. By recrystallization from xylene 6.4 g. (44%) of 1,2,3,4,5,6-tribenzanthracene was obtained; m. p. 225–228°. Fieser and Dietz[7] obtained a 24% yield of the hydrocarbon melting at 224° by pyrolysis of the ketone without the addition of zinc dust.

Preparation of the 9,10-Dihydro Derivatives of the Polycyclic Hydrocarbons.—A mixture of 0.5 g. of the hydrocarbon, 1 g. of powdered sodium, 50 cc. of anhydrous ether, 50 cc. of dry benzene and a few sharp particles of glass[8] was shaken in absence of air for two days. The intense color which formed after a few minutes usually was replaced by still another color, that of the 9,10-disodium addition compound. After the color had been completely discharged by addition of methanol, the solution was separated from the excess of sodium, shaken with dilute hydrochloric acid, filtered and evaporated. The dihydro compound which remained was then recrystallized.

For the reaction with lithium, the same procedure was

(3) Schlenk and Bergmann, *Ann.*, **463**, 134 (1928).
(4) Bachmann and Pence, THIS JOURNAL, **57**, 1130 (1935).
(5) Morgan and Coulson, *J. Chem. Soc.*, 2203 (1929).
(6) Clar, *Ber.*, **62**, 1574 (1929).
(7) Fieser and Dietz, *ibid.*, **62**, 1827 (1929).
(8) Compare Bachmann and Wiselogle, THIS JOURNAL, **58**, 1943 (1936).

used except that 0.8 g. of lithium wire (0.5 mm. diameter) was employed. The reaction was initiated by pressing the lithium wire in several places with a glass rod. The mixture was then shaken for five to seven days.

9,10 - Dihydro - 5 - methyl - 1,2 - benzanthracene obtained from the intensely wine-red disodium addition product of 5-methyl-1,2-benzanthracene crystallized from acetone–ethanol in thin, colorless plates; yield 57%; m. p. 128–129.5°.

Anal. Calcd. for $C_{19}H_{16}$: C, 93.4; H, 6.6. Found: C, 93.5; H, 6.5.

9,10 - Dihydro - 5 - phenyl - 1,2 - benzanthracene obtained from the brownish-purple disodium compound of 5-phenyl-1,2-benzanthracene[9] crystallized from acetic acid in glistening, colorless needles; yield, 90%; m. p. 96–96.5°.

Anal. Calcd. for $C_{24}H_{18}$: C, 94.1; H, 5.9. Found: C, 94.4; H, 6.0.

9,10-Dihydro-1,2,3,4-dibenzanthracene obtained from the dark lavender disodium addition compound of 1,2,-3,4-dibenzanthracene crystallized from benzene–ethanol in colorless needles; yield 84%; m. p. 202–203°. The identical compound was obtained in 64% yield from the purple dilithium addition compound of the hydrocarbon.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.2; H, 5.8. Found: C, 93.8; H, 6.1.

9,10 - Dihydro - 6 - methyl - 1,2,3 4 - dibenzanthracene was obtained in 80% yield from both the reddish-purple disodium compound and the bluish-purple dilithium compound of 6-methyl-1,2,3,4-dibenzanthracene. It crystallized from benzene in fine, colorless needles; m. p. 207–209.5°.

Anal. Calcd. for $C_{23}H_{18}$: C, 93.8; H, 6.2. Found: C, 93.6; H, 6.3.

9,10 - Dihydro - 1,2,3,4,5,6 - tribenzanthracene, obtained from the dark blue disodium compound of 1,2,3,4,5,6-tribenzanthracene in 73% yield and from the blue dilithium derivative in 40% yield, crystallized from xylene in colorless needles; m. p. 281–283°.

Anal. Calcd. for $C_{26}H_{18}$: C, 94.5; H, 5.5. Found: C, 94.1; H, 5.6.

The mixture of compounds obtained from the bluish-green sodium addition compound of 1,2,6,7-dibenzanthracene and methanol melted at 170–200°. From the bluish-green lithium addition product a 73% yield of one of the two possible **dihydro-1,2,6,7-dibenzanthracenes** was isolated as fine, colorless needles; m. p. 157–160.5°. It was not possible to determine whether this compound was the 5,8- or the 9,10-dihydro derivative.

Anal. Calcd. for $C_{22}H_{16}$: C, 94.2; H, 5.8. Found: C, 94.2; H, 5.8.

Dehydrogenation of the 9,10-Dihydro Derivatives.—A mixture of 50 mg. of the dihydro derivative and 10 mg. of sulfur was heated at 200–230° for one hour. The product was dissolved in toluene and the solution was shaken with mercury for several hours in order to remove the excess of sulfur. From the solution the parent hydrocarbon was isolated in good yield. Thus, a 78% yield of 1,2,3,4-dibenzanthracene was obtained by dehydrogenation of 9,10-dihydro-1,2,3,4-dibenzanthracene.

Oxidation of the 9,10-Dihydro Derivatives.—A solution of 50 mg. of the 9,10-dihydro derivative and slightly more than the calculated amount of sodium dichromate dihydrate in 10 cc. of acetic acid was heated at the boiling point for forty-five minutes. The 9,10-dione, which precipitated on adding dilute sulfuric acid to the mixture, was purified by sublimation at 0.2 mm., followed by recrystallization from acetic acid. In each case, the 9,10-dione proved to be identical with the quinone obtained by oxidizing the parent hydrocarbon. For example, from 9,10-dihydro-1,2,3,4-dibenzanthracene a 77% yield of 1,2,3,4-dibenzanthraquinone was obtained, which was identical with the product formed by oxidation of 1,2,3,4-dibenzanthracene.

Our 1,2,3,4,5,6-tribenzanthraquinone melted at 246.5–247.5°, while the reported value[7] is 244°. Oxidation of the dihydro-1,2,6,7-dibenzanthracene (m. p. 157–160.5°) gave a mixture of quinones of the same nature as that obtained by oxidation of 1,2,6,7-dibenzanthracene.

Reaction of the Alkali Addition Compounds with Carbon Dioxide.—Carbon dioxide (dried by concentrated sulfuric acid and phosphorus pentoxide) was passed into a cooled solution of the 9,10-disodium or 9,10-dilithium addition compound of the hydrocarbons until the color of the mixture was discharged completely. The suspension of the alkali salt of the carboxylic acid was decanted from the excess of the metal and was shaken with ice water. Acidification of the separated aqueous solution precipitated the carboxylic acid, which was then recrystallized. The ether–benzene solution from which the sodium salt had been extracted always yielded a small amount of the 9,10-dihydro derivative but none of the parent hydrocarbon. The methyl esters of the acids were all prepared by means of diazomethane.

9,10-Dicarboxy-9,10-dihydro-1,2-benzanthracene, obtained from the dilithium addition compound of 1,2-benzanthracene, formed thin, colorless sheets from acetone–benzene; yield 58%; m. p. 252° with evolution of gas.

Anal. Calcd. for $C_{20}H_{14}O_4$: C, 75.4; H, 4.4. Found: C, 75.4; H, 4.8.

The **dimethyl ester** crystallized from acetone–ethanol in clusters of thick, colorless plates; m. p. 143.5–145°.

Anal. Calcd. for $C_{22}H_{18}O_4$: C, 76.3; H, 5.2. Found: C, 76.1; H, 5.4.

In one run the disodium addition compound gave a crystalline acid but in half a dozen other runs the acid and the methyl ester derived from it proved to be uncrystallizable oils.

9,10-Dicarboxy-9,10-dihydro-1,2,3,4-dibenzanthracene, obtained from the dilithium compound of 1,2,3,4-dibenzanthracene, crystallized from xylene in clusters of colorless prisms; yield 65%; m. p. 270–274° with evolution of gas. The acid was analyzed in the form of its **dimethyl ester,** which crystallized from acetone–ethanol in colorless prisms; m. p. 236–238°.

Anal. Calcd. for $C_{26}H_{20}O_4$: C, 78.8; H, 5.1. Found: C, 78.7; H, 5.3.

The 9-carboxy-9,10-dihydro-1,2,3,4-dibenzanthracene,

(9) Bachmann and Bradbury, *J. Org. Chem.*, **2**, 175 (1937).

which was obtained from the sodium addition compound in 24% yield, crystallized from acetone–xylene in colorless plates; m. p. 227.5–230° with evolution of gas. Since the acid was difficult to purify, it was converted to its **methyl ester** for analysis. The ester crystallized from acetone ethanol in clusters of colorless prisms; m. p. 158–164°.

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.2; H, 5.4. Found: C, 84.3; H, 5.4.

9,10-Dicarboxy-9,10-dihydro-1,2,5,6-dibenzanthracene (IV), obtained from the dilithium addition compound of 1,2,5,6-dibenzanthracene in 59% yield, crystallized from acetone–benzene in clusters of colorless prisms; m. p. 262–264° with gas evolution. The acid is very soluble in acetone but only slightly soluble in benzene. It was analyzed in the form of its **dimethyl ester,** which crystallized from acetone–ethanol in stout, colorless needles; m. p. 255–257°.

Anal. Calcd. for $C_{26}H_{20}O_4$: C, 78.8; H, 5.1. Found: C, 78.1; H, 5.0.

The reaction between the disodium compound of 1,2,5,6-dibenzanthracene and carbon dioxide did not always proceed in the same manner. Usually a 60–70% yield of an acid was obtained which crystallized from benzene in colorless needles; m. p. 242–255° with decomposition. Since the acid was difficult to purify, it was converted to its **methyl ester,** which crystallized from benzene–methanol in broad, colorless needles; m. p. 174–175°. Although the ester was not obtained quite pure, analysis showed that the acid was **9-carboxy-9,10-dihydro-1,2,5,6-dibenzanthracene** (V).

Anal. Calcd. for $C_{24}H_{18}O_2$: C, 85.2; H, 5.4. Found: C, 84.1; H, 5.3.

In some runs the disodium compound yielded the same dicarboxylic acid that was obtained from the dilithium addition compound. In one run there was obtained a 79% yield of an acid, m. p. 255–258°, whose methyl ester crystallized in broad, colorless needles which melted at 100–101°. Unfortunately, this product was all used up in certain tests and we were unable to secure any more of it in subsequent experiments.

6,12b-Dicarboxy-6,12b-dihydro-3-methylcholanthrene (VI), was obtained in 42% yield from the dilithium addition compound of 3-methylcholanthrene.[2] From hot benzene the dicarboxylic acid separated in brownish-yellow crystals; m. p. 242–246°. Considerable losses were experienced in the process of recrystallization, for the acid appeared to be unstable. Its **dimethyl ester** crystallized from acetone–methanol in clusters of short, brownish prisms; m. p. 205–208°.

Anal. Calcd. for $C_{25}H_{22}O_4$: C, 77.7; H, 5.7. Found: C, 77.1; H, 5.9.

The acid isolated in 59% yield from the disodium addition product crystallized in pale yellow needles; its **methyl ester** formed pale yellow cubes from acetone–methanol; m. p. 178–179°. Analysis of the latter showed that the acid was a **monocarboxy-6,12b-dihydro-3-methylcholanthrene,** but whether the carboxyl group was in the 6- or 12b-position was left undecided.

Anal. Calcd. for $C_{23}H_{20}O_2$: C, 84.1; H, 6.1. Found: C, 83.9; H, 5.5.

Summary

The reaction between a number of polycyclic hydrocarbons with sodium and with lithium has been investigated. From the intensely colored alkali metal addition compounds of the hydrocarbons the dihydro derivatives were obtained by treatment with methanol. With carbon dioxide the addition compounds yielded salts of carboxylic acids.

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